

Electron Beam Excitation Studies of Potential Dye Vapor Phase Laser Systems*

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Abstract. Excitation processes of selected dye vapor-rare gas mixtures pumped by an electron beam have been studied. These experiments revealed the importance of effective collisional electron energy transfer pumping via a dense rare gas rather than a radiative energy transfer from an excimer laser gas mixture to achieve population inversion in an organic dye vapor.

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The development of tunable laser sources operating at near ultraviolet wavelengths is a topic of growing interest. This has stimulated various approaches which include gaseous excimer lasers [1], nonlinear optical devices [2], and attempts to extend the operating region of dye lasers beyond the existing short wavelength limit of 340 nm. Although excimer UV lasers are very efficient fixed-frequency optical sources they require additional Raman or dye laser devices for the generation of tunable radiation.

In this paper we describe fluorescence studies on several electron beam pumped dye vapors and dye vapor-rare gas mixtures which were performed to establish optimum conditions for electron beam excited dye vapor lasers. This investigation is of particular importance, since, in spite of successful operation of optically pumped dye vapor lasers [3, 4] so far it has not been possible to achieve laser action in either electrical discharge or electron beam pumped dye

vapors [5, 6]. When a dye vapor is excited by an electron beam, molecular decomposition of the dye due to high energy electron impact is a potential problem. This suggests finding a buffer gas system capable of minimizing dye fragmentation and permitting efficient energy transfer to the dye. Electron beam excitation has been a particularly effective pump source for rare gas monohalide lasers. This in turn led to successful fast discharge excitation and subsequently to regular discharge pumping of rare gas halides [7, 8]. We anticipate a similar development for organic dye vapors provided it is possible to find an optimized buffer gas-dye vapor lasing mixture. Therefore, we have studied in detail the excitation processes of three selected dyes, POPOP, *p*-terphenyl and the xanthene dye N-92 by monitoring the electron beam excited fluorescence of (i) the pure dye vapor with a small quantity of neutral buffer gas added to prevent fogging of the optical windows, (ii) a dye vapor-high atomic number rare gas mixture, such as xenon ($Z = 54$), and (iii) a dye vapor-buffer gas mixture where the buffer gas can produce intense UV

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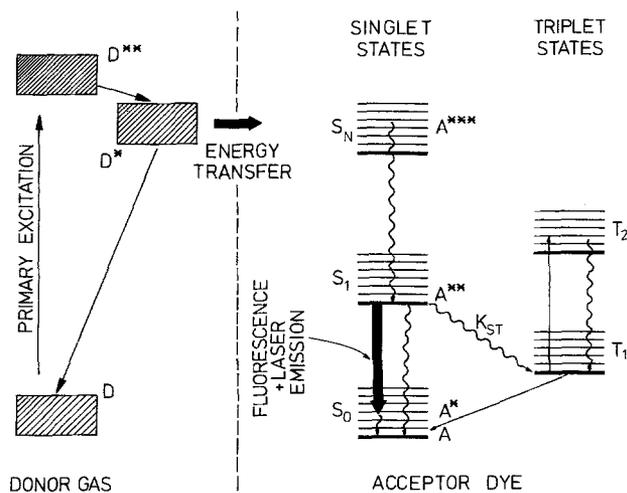
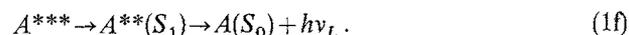
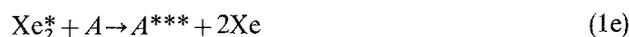


Fig. 1. Relevant energy level scheme of buffer gas-dye vapor mixture

laser emission. In particular, we have used KrF [9, 10], XeF [11], and Ar-N₂ mixtures [12, 13], for which we expect both efficient shielding of the dye structure against fragmentation and efficient energy transfer of radiation via dipole-dipole interactions [14], provided the presence of appreciable amounts of dye vapor molecules does not disturb the resonant character of the energy transfer mechanisms of the rare buffer gas system itself. We may assume a somewhat simplified energy level diagram for the donor buffer gas and acceptor dye vapor species, as shown in Fig. 1. From this figure we may postulate some of the characteristics of such a system which must be optimized for laser action with electron beam excitation. Good donor and acceptor gas characteristics include: (i) high stopping power (i.e., large electron beam captive cross section which is also a function of pressure); (ii) energy of donor should be concentrated in D^* state; (iii) energy difference between D^{**} and D^* should be small; (iv) lifetime of D^* should be long; (v) energy of state D^* should be nearly equal to the energy of state A^{***} ; (vi) collision cross section between A^{**} and D should be small; and (viii) collision cross section between A^* and D should be large. Based on the above criteria xenon appears to be a good candidate as a donor gas. It has the highest stopping power of all the rare gases and in this case D^{**} , the atomic ion, and D^* , the Xe_2^* excimer, are closely spaced. For excitation levels up to a few A/cm^2 efficiencies as high as 30% have been reported for rare gas excimers [15].

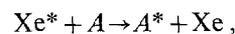
The right-hand side of Fig. 1 shows a typical energy level diagram of a laser dye [16] with radiationless

transitions $A^{***}(S_N) - A^{**}(S_1)$ and $A^*(S_0) - A(S_0)$ included. Possible suppression of potential laser action in the singlet system by triplet-triplet absorption has been added [16]. In the case of buffer gas excitation the triplet system can be populated by both, intersystem crossing with a rate constant k_{ST} (which should be of minor importance due to the short duration of the excitation) and already initially by non spin-selective collision processes. In examining the kinetics for a dye system using a xenon buffer we propose the following plausible excitation process for transforming energy to the acceptor dye



The first three reactions are known to be rapid for pressures greater than 1 atm and excitation levels of a few A/cm^2 . Under such conditions three body molecular association, Eq. (1d), is the limiting reaction for excimer formation; and the formation time is less than 4 ns for pressures greater than 4 atm. The lifetimes for $\text{Xe}_2^*(O_u^+)$ and $\text{Xe}_2^*(1_u)$ are 6 ns and 100 ns, respectively [17]. It has been recently shown that these states are rapidly mixed by electrons [18] and should act as a single state at high electron densities radiating with a lifetime of about 20 ns for conditions of electron beam excitation. This lifetime should be sufficiently long for efficient energy transfer (1e) to the dye vapor. Of the rare gases we expect the xenon excimer to have the largest transfer cross section as its deexcitation energy most nearly matches the singlet-singlet transition energy of the dyes investigated.

Excitation transfer is also possible from excited atomic species in the reaction



where A is a dye molecule. At this time, we feel this process should be less favorable than transfer from the excimer because of the desirability of matching the dye's absorption bands. The ratio of transfer from atomic states to that from excimers is given by the ratio of the above reaction rate to the rate of molecular formation described by (1d). At sufficiently high xenon pressure energy transfer will occur predominantly from excimers.

1. Apparatus

The key element in the development of electron beam pumped dye vapor lasers is a suitable reaction cell with both electron and optical beam access. This cell must be capable of high pressure and temperature operation. The experimental arrangement is similar to that reported earlier for the fluorescence studies of electron-beam pumped POPOP dye vapor [6]. The present cell configuration shown in Fig. 2 allows gas pressures of up to 5 atm and temperatures up to 450° C. Such high temperatures have been shown to be necessary [3, 4] to produce vapor pressures between 10 to 100 Torr for optically pumped dye vapor lasers. These vapor pressures correspond to the usual concentration range of 10^{-4} to 10^{-3} moles/liter of liquid solution lasers. The actual vapor pressure curves of N-92 and POPOP are reported in [3], for *p*-terphenyl in [19].

Furthermore, pressures of a few atmospheres have proven adequate for efficient operation of the excimer lasers. The stainless steel cell shown in Fig. 2 is placed directly behind the field emission cathode-anode assembly of a Physics International Pulserad 110 electron-beam accelerator. The reaction cell is equipped with two high pressure and temperature resistant sapphire windows and gas handling connections for mixing of different buffer gases. An oven with provision for optical access and temperature monitoring can be placed over the dye cell. A 1 MeV, 20 kA, 20 ns electron beam is coupled into the excitation region transverse to the optic axis through a 25 μ m thick Havar® foil window of 8×1 [cm] cross sectional area. A Rogowski coil surrounds the graphite cathode for monitoring the electron beam flux. Technical details of the cathode-anode construction are shown in Fig. 3. From the burn pattern on the Havar foil, it could be established that a knife-edge shaped cathode placed 12 mm from the anode window produced a very narrow excitation profile. In order to optimize the performance of the electron beam accelerator it was necessary to find a compromise of relatively long life-time for the anode foil, effective electron beam transmission through the anode foil and optimum impedance matching of the diode to the Blumlein discharge network of the electron beam accelerator. With an anode-cathode spacing of 12 mm reliable results were obtained for at least 20 shots of the accelerator, which is sufficient to obtain on the average two series of fluorescence data as described in the following section. The optical emission of the dye

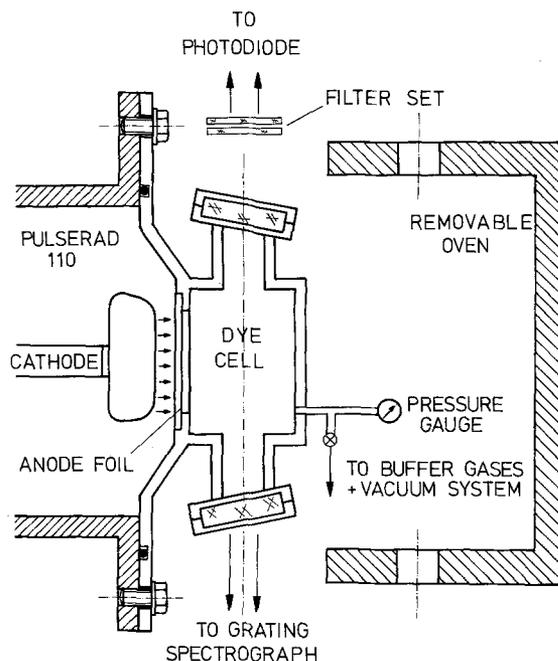


Fig. 2. Schematic diagram of the apparatus

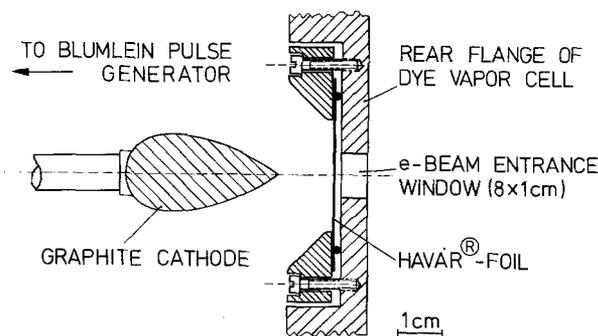


Fig. 3. Technical details of field emission diode of electron-beam accelerator

vapors was monitored simultaneously by a grating spectrograph and a fast-risetime Valvo UVHC 20 photodiode whose output was observed on a Tektronix 7904 oscilloscope. In order to differentiate between the pump radiation of the buffer gas and the dye fluorescence suitable cut-off filters were used.

2. Experimental Results

2.1 Xanthene Dye N-92

An interesting dye for potential laser action is the xanthene dye N-92, because its absorption band perfectly matches the emission range of the Ar-N₂

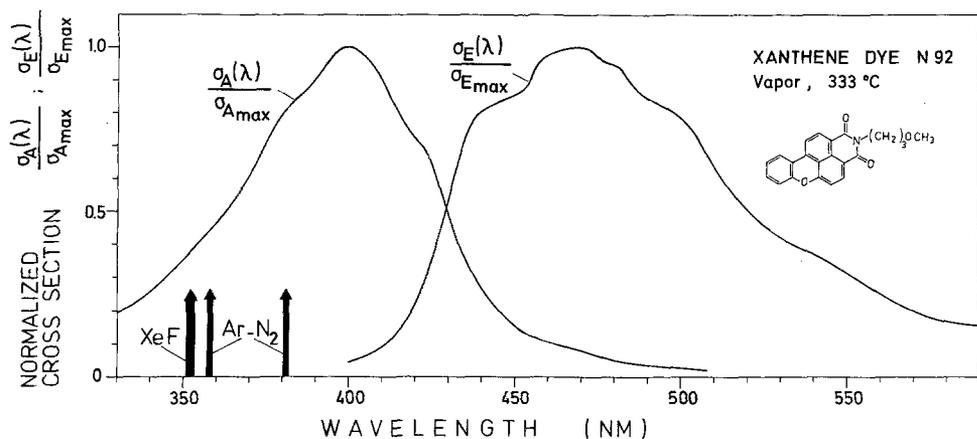


Fig. 4. Normalized absorption and fluorescence of xanthene dye N-92 in the vapor phase [3] with spectral position of XeF and Ar-N₂ lines indicated

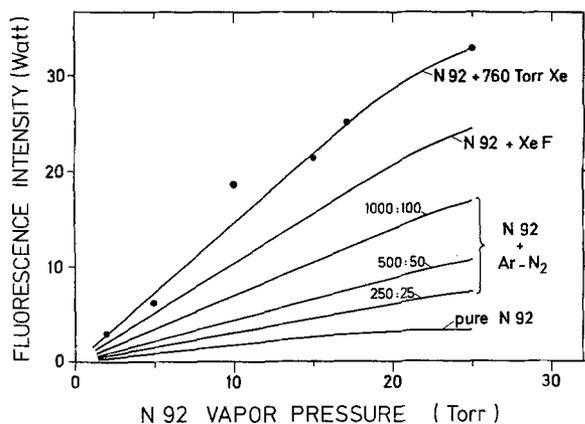


Fig. 5. N-92 fluorescence intensity versus vapor pressure for pure N-92 vapor and several dye vapor-buffer gas mixtures. The Ar-N₂ mixture ratios indicated refer to pressure ratios in Torr. Data points to demonstrate typical scatter of the measured fluorescence intensities are given for the system N-92 + xenon as an example

and XeF laser systems (see Fig. 4) [3]. Fluorescence data of N-92 were taken at 460 nm or longer wavelengths to avoid interferences with electron beam excited background radiation of the empty cell near 420 nm. Electron-beam excitation of N-92 dye vapor revealed intense fluorescence whose dependence on vapor pressure as derived from temperature measurements is plotted in Fig. 5. All fluorescence intensities were measured with a calibrated photodiode of 24 mm entrance window diameter in a constant distance of 30 cm from the center of the dye cell. In all cases the fluorescence intensity increases linearly with pressure. A slight saturation is evident at temperatures approaching 380° C. At this temperature break-

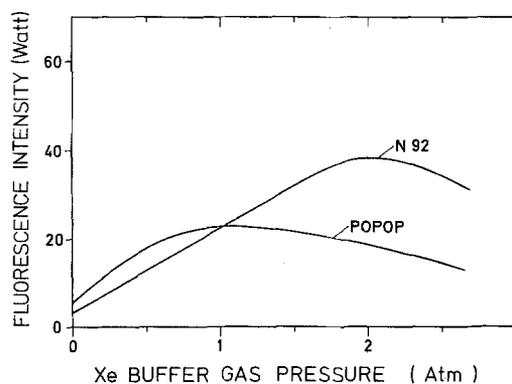


Fig. 6. Saturation behavior of N-92 and POPOP fluorescence in the presence of Xe buffer gas (dye vapor pressure \approx 15 Torr)

down of the molecular structure seems to occur. This transition is irreversible, since the fluorescence does not reappear at lower temperatures. This observation is in agreement with a proposed explanation for the observed discontinuity in the vapor pressure curve of this dye by Schäfer and Steyer [3]. Furthermore, Fig. 5 shows that the N-92 fluorescence increases more than 10 fold in the presence of Xe buffer gas. From Fig. 5 we may also conclude that collisional energy transfer from Xe to the dye is more efficient than radiation transfer from known rare gas-halide laser mixtures, such as XeF [11] or Ar-N₂ [12]. The XeF laser mixture was prepared according to [11] by using a mixture of Ar, Xe, and NF₃ in the ratio of 250 : 25 : 1 at a total pressure at room temperature of 1 atm. The presence of XeF obviously enhances the N-92 fluorescence to a higher degree than expected

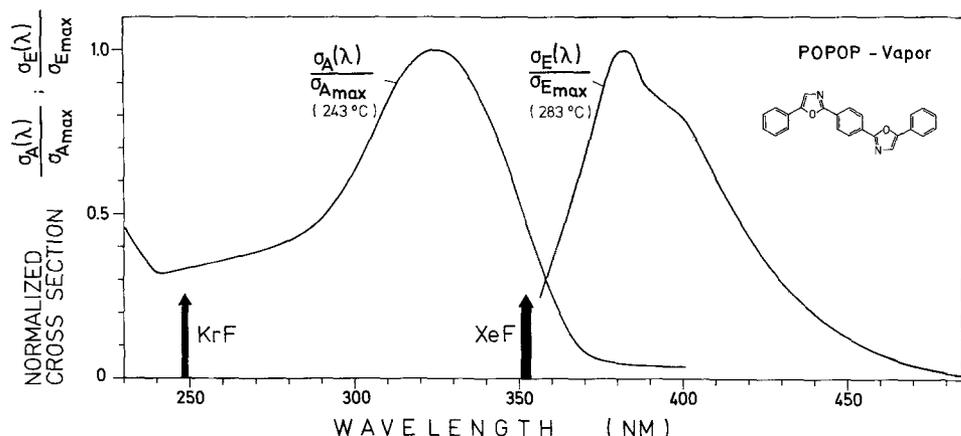


Fig. 7. Normalized absorption and fluorescence of POPOP vapor [3] with spectral position of KrF and XeF lines indicated

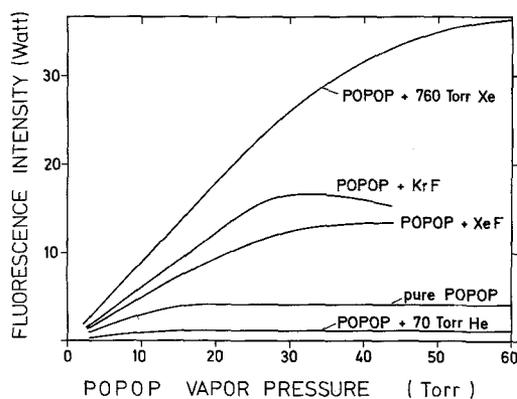


Fig. 8. POPOP fluorescence intensity versus vapor pressure for pure POPOP vapor and several dye vapor-buffer gas mixtures

from the Xe content of the mixture as compared with the addition of pure Xe. This may be partially due to the large amount of Ar present, which has been proven to be nearly as effective in energy transfer as Xe [6]. Compared to XeF, Ar-N₂ mixtures are less effective in generating the N-92 fluorescence at intermediate pressures. From the linear increase of the fluorescence with increasing Ar-N₂ pressure at a constant ratio of 10:1, as depicted in Fig. 5, we conclude that this mixture could in principal enhance the dye fluorescence by the same order of magnitude as Xe, provided the cell construction can withstand the high pressures required for an equivalent stopping power. We also measured the N-92 fluorescence intensity as a function of Xe pressure. As shown in Fig. 6, the dye intensity increases with increasing xenon pressure reaching a maximum at approximately

2 atm. There are several possible kinetic models which explain this behavior; and we are currently trying to determine experimentally which one is most probable.

An additional observation is that the usually observed strong hypsochromic shift of fluorescence from dyes in the vapor phase compared to dyes in solution decreases with increasing Xe buffer gas pressure.

2.2. POPOP

The most promising dye in the vapor phase investigated by us so far is the dye POPOP [*p*-phenylenebis-(5-phenyl-2-oxazole)]. It is photochemically stable at elevated temperatures which is a prerequisite for long-term laser operation and its fluorescence peak for a dye vapor-buffer as mixture is centered around 390 nm. The POPOP absorption and fluorescence spectra together with the spectral position of the applied KrF and XeF pump source are shown in Fig. 7. The fluorescence intensity, observed within the spectral range of 30 nm centered at 360 nm, is plotted as a function of vapor pressure for pure POPOP vapor and various buffer gases in Fig. 8. Apart from the linear increase of the POPOP fluorescence with POPOP vapor pressure up to 15 Torr, it is interesting to note that the KrF supported dye fluorescence breaks down completely at higher vapor pressure. This behavior is probably a consequence of the small amount of NF₃ present in the system (He, Kr, and NF₃ were mixed in a ratio of 500:50:1 according to [7] with a total pressure of 1 atm), which can no longer compete with the high pressure of POPOP. In addition to shielding of the resonant

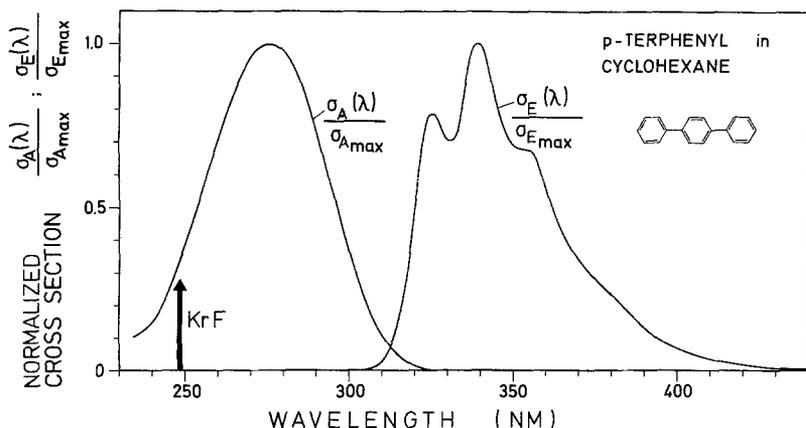


Fig. 9. Normalized absorption and fluorescence of *p*-terphenyl in cyclohexane solution [23] with spectral position of KrF laser line indicated

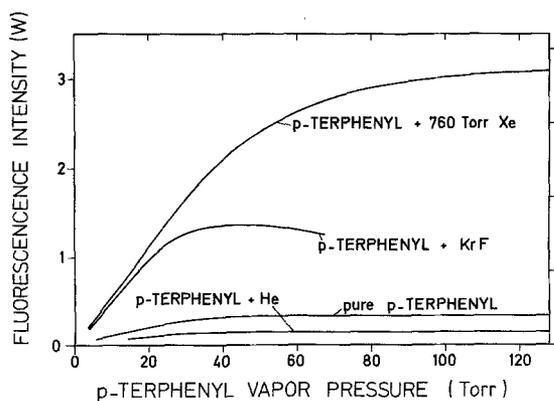


Fig. 10. *p*-Terphenyl fluorescence intensity versus vapor pressure for pure *p*-terphenyl and two dye vapor-buffer gas mixtures

energy, transfer in the rare gas-halide system by the presence of appreciable amounts of dye vapor, the addition of He finally quenches the dye fluorescence, as shown by the reduced fluorescence intensity of the system POPOP + He (cf. Fig. 8 and [Ref. 6, Fig. 3]). As has been already shown in Fig. 6, the electron-beam excited fluorescence of POPOP vapor cannot be enhanced indefinitely by the addition of Xe buffer gas; at the same dye vapor pressure as N-92 (15 Torr) the POPOP fluorescence reaches its maximum value at a lower Xe buffer gas pressure than required for N-92.

2.3. *p*-Terphenyl

p-Terphenyl has a fluorescence range which covers the potentially useful 300 to 360 nm range of the UV spectrum and is convenient to use in the vapor phase due to its high vapor pressure: heating up the dye cell to 208°C produces a vapor pressure of 10 Torr [19]. Although optical excitation from the fourth harmonic output from a Nd³⁺ glass laser causes intense UV

emission from *p*-terphenyl [20], laser action in the vapor phase has not yet been observed. Recent progress on the excitation of this dye in liquid solution by a novel plasma focus technique shows it to be an efficient dye for a high power dye laser in the UV spectral range [21, 22]. Figure 9 shows the fluorescence and absorption characteristics for this dye in cyclohexane solution [23] together with the spectral position of the KrF pump source. The spectral range of 30 nm centered at 360 nm was selected to ensure adequate sensitivity of the recording photographic material (Polascope film type 410).

It was found (Fig. 10) that the very weak fluorescence of pure *p*-terphenyl vapor, compared to the dyes N-92 and POPOP, could not be enhanced to the same degree of brightness by the addition of a KrF mixture and other buffer gases. In fact, as soon as the dye vapor pressure exceeded 40 Torr corresponding to 270°C, the intense KrF radiation was quenched, as observed previously for the POPOP: Ar-N₂ mixture [6] and for POPOP: KrF. Even the presence of pure Xe gas, which exhibits the most effective buffer gas properties in the case of the two other vapor dyes, led to saturation of the *p*-terphenyl fluorescence, although the de-excitation energy of the Xe₂^{*} dimer (7.2 eV) matches better the required energy of 4.6 eV for population of the first excited singlet state of *p*-terphenyl compared to the other dyes investigated. This might be a consequence of an increased inter-system crossing rate k_{ST} in *p*-terphenyl due to the large heavy-atom effect of Xe [24].

3. Conclusions

The successful generation of intense dye vapor fluorescence by relativistic electron bombardment via a suitable buffer gas demonstrates the feasibility of

electron beam pumping of complex organic dyes in the vapor phase. From the spectral profile of the fluorescence of the three dyes studied so far with an ultraviolet absorption range from 220 to 390 nm, details of the energy transfer mechanism for the xenon buffer gas can be inferred. A close energy match of the dye vapor absorption peak to the de-excitation energy of the Xe_2^* excimer (7.2 eV) does not appear to be essential [15, 25], since this would in fact suggest that *p*-terphenyl would fluoresce stronger than POPOP (singlet-singlet transition energy $S_1 \rightarrow S_0$ 3.8 eV) or N-92 (singlet-singlet transition energy $S_1 \rightarrow S_0$ 3.1 eV). However, the strong fluorescence intensity obtained for electron beam excited N-92 indicates that the electron stopping power of Xe (the rare gas used in these experiment with the highest atomic number) makes it an attractive buffer gas. The stopping behavior of various rare-gases and pure POPOP dye vapor is given in Table 1 as determined from energy loss calculations for 1 MeV electrons after passage through a 4 cm layer of the gas in question at a pressure of 100 Torr [26, 27]. It should be pointed out that the linear dependence of energy loss on gas pressure is an approximation only valid for a low electron flux density, which is not the case when using high current pulse excitation from the Pulserad 110 accelerator. The calculated stopping powers of Table 1 are primarily based upon electron-electron interaction, leading to various ionization processes of the dye vapor and the buffer gas. Up to an electron energy of 1 MeV energy loss due to the generation of bremsstrahlung is of minor importance [28]. Relativistic e-beam propagation has been studied in detail in [29, 30], taking into account space-charge repulsion, space-charge neutralization and beam constriction due the self-magnetic field of an intense electron beam. Even the simple stopping power calculation of Table 1 indicates that approximately 10^{17} Xe_2^* dimers can be produced by an energy loss of only 2% within an active volume of 200 cm^3 . It is interesting to note that about the same number of dye molecules is present in this volume. The assumption, that the number of Xe dimers has to match the number of dye molecules present in the active volume, is supported by the observation of a dye-vapor-pressure dependent optimal buffer gas pressure (Fig. 6). The feasibility of enhanced excitation of the dye vapors through radiation transfer from rare gas halide excimer systems was examined in some detail. However, quenching of the excimer fluorescence by the dye vapor seems to preclude any significant amount of radiation

Table 1. Energy loss [%] of the rare gases Xe, Ar, and He and of N_2 and POPOP vapor at a pressure of 100 Torr for 1 MeV electrons after passage through a layer of 4 cm thickness. For POPOP the total number of electrons of the molecule has been taken into consideration

Gas, Vapor	Energy Loss [%]
Xe	0.34
Ar	0.12
He	0.02
N_2	0.10
POPOP	1.00

transfer. This type of quenching is similar to that reported recently [31] for XeF^* and KrF^* spontaneous emission behavior observed with helium and xenon or krypton-fluorine gas mixtures. A possible reason for the suppression of the excimer radiation is the presence of dye vapor in larger amounts than NF_3 . Thus it is possible for the dye vapor to shield the NF_3 , in addition to absorption of the primary rare gas fluorescence. Of all the mixtures studied, only N-92 and Ar- N_2 mixtures seem to show partial radiative energy transfer. This may be due to the fact that the buffer gas mixture contains a higher concentration of the minor component (N_2) as compared with the fraction of NF_3 in the rare gas mixtures.

In summary, the optimum conditions for spontaneous emission of electron-beam excited dye vapor-buffer gas mixtures in our experimental arrangement have been established. The presence of xenon gas up to a pressure of about 2 atm appears to produce the best fluorescence enhancement. So far internal radiation transfer processes have not been effective in the excitation of vapor phase dye lasers, since the presence of even small amounts of dye vapor inhibits the excitation mechanism of the efficient rare gas halide excimer systems. However, it may eventually be possible to utilize radiative excitation by operating with NF_3 pressures that are at least 10 times greater than the dye vapor pressure. Work is now in progress to establish the feasibility of electron beam-pumped vapor phase dye lasers based on these experimental observations.

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